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Anna I. Krylov	
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	5f. WORK UNIT NUMBER

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14. ABSTRACT

The main goal was to develop electronic structure methods targeting electronic states that are metastable with respect to electron detachment, to aid computational studies of fundamental chemical processes involving molecules and radicals in highly excited and ionized electronic states. The specific aims are to develop and calibrate complex-scaled equation-of-motion coupled cluster (cs-EOM-CC) and CAP (complex absorbing potential) augmented EOM-CC methods. We have implemented and benchmarked cs-EOM-CCSD and CAP-augmented EOM-CCSD methods for excitation energies and electron attachment. We investigated the performance

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Report Title

Final Report: Metastable autoionizing states of molecules and radicals in highly energetic environment

ABSTRACT

The main goal was to develop electronic structure methods targeting electronic states that are metastable with respect to electron detachment, to aid computational studies of fundamental chemical processes involving molecules and radicals in highly excited and ionized electronic states. The specific aims are to develop and calibrate complex-scaled equation-of-motion coupled cluster (cs-EOM-CC) and CAP (complex absorbing potential) augmented EOM-CC methods. We have implemented and benchmarked cs-EOM-CCSD and CAP-augmented EOM-CCSD methods for excitation energies and electron attachment. We investigated the performance of CAP-EOM-CCSD for various molecular shape resonances. By analyzing analytic energy expression, we discovered a simple yet efficient de-perturbative correction that eliminates the unphysical perturbation due to the finite-strength CAP. Our version of CAP-EOM-CCSD has shown robust performance, improved accuracy, and decreased dependence on the CAP onset parameters. We also tested this approach for potential energy curves. Unlike the original versions of CAP methods, our 1st order corrected CAP-EOM-CCSD yields smooth and internally consistent potential energy curves. We extended the methodology to describe properties of resonance states by implementing Dyson orbitals and transition dipole moments. We also applied this methodology to recent experimental results on resonances.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received		Paper
03/18/2016	6.00	Thomas-C. Jagau, Anna I. Krylov. Characterizing metastable states beyond energies and lifetimes: Dyson orbitals and transition dipole moments, J. Chem Phys., (02 2016): 54113. doi:
03/22/2016	7.00	Thomas-C. Jagau, Diep B. Dao, Nicholas S. Holtgrewe, Anna I. Krylov, Richard Mabbs. Same but Different: Dipole-Stabilized Shape Resonances in CuF? and AgF?, J.. Phys. Chem. Letters, (06 2015): 2786. doi:
08/01/2013	2.00	Dmitry Zuev, Evgeny Epifanovsky, Anna I. Krylov, Ksenia B. Bravaya. Complex-scaled equation-of-motion coupled-cluster method with single and double substitutions for autoionizing excited states: Theory, implementation, and examples, The Journal of Chemical Physics, (2013): 0. doi: 10.1063/1.4795750
08/29/2014	3.00	Thomas-C. Jagau, Dmitry Zuev , Ksenia B. Bravaya, Evgeny Epifanovsky, Yihan Shao, Eric Sundstrom, Martin Head-Gordon, Anna I. Krylov. Complex absorbing potentials within EOM-CC family of methods: Theory,implementation, and benchmarks, J. Chem. Phys., (07 2014): 24102. doi:
08/29/2014	4.00	T.C. Jagau, A.I. Krylov. Complex Absorbing Potential Equation-of-Motion Coupled-Cluster Method Yields Smooth and Internally Consistent Potential Energy Surfaces and Lifetimes for Molecular Resonances, J. Phys. Chem. Lett., (08 2014): 3078. doi:
08/29/2014	5.00	R. Benny Gerber, Anna I. Krylov, Barak Hirshberg. Calculations predict a stable molecularcrystal of N8, Nature Chemistry, (01 2014): 52. doi:

TOTAL: **6**

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

<u>Received</u>   <u>Paper</u>

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

The results of the ARO-supported research were presented at numerous meetings and university seminars. All the presented results were published in peer-reviewed publications (uploaded).

Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

<u>Received</u>   <u>Paper</u>

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

<u>Received</u>   <u>Paper</u>

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

<u>Received</u>   <u>Paper</u>

TOTAL:

Number of Manuscripts:

Books

<u>Received</u>   <u>Book</u>

TOTAL:

<u>Received</u>   <u>Book Chapter</u>

TOTAL:

Patents Submitted

Patents Awarded

Awards

2016 Phi Kappa Phi Faculty Recognition Award (USC);
2015 Elected Member, International Academy of Quantum Molecular Science;
2015 Fellow, American Chemical Society;
2015 INSIGHT Into Diversity Inspiring Women in STEM Award;
2013 Melon Mentoring Award (USC);
2013 Coulson Lecturer (UGA);
2012 Lowdin Lecturer (Uppsala);
2012 Fellow, American Association for the Advancement of Science;
2012 ACS Physical Chemistry Division Award in Theoretical Chemistry.

Graduate Students

NAME	PERCENT_SUPPORTED	Discipline
Dmitri Zuev	0.50	
Arman Sadybekov	0.25	
FTE Equivalent:	**0.75**	
Total Number:	**2**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
Thomas Jagau	0.25
Matthias Schneider	1.00
FTE Equivalent:	**1.25**
Total Number:	**2**

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Anna Krylov	0.08	
FTE Equivalent:	**0.08**	
Total Number:	**1**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields: 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields: 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale): 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering: 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: 0.00

Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PHDs

NAME
Dmitri Zuev

Total Number: 1

Names of other research staff

NAME   PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

The most important achievement is efficient production-level implementation of cs-EOM-CCSD (EE and EA variants) and CAP-EOM-CCSD (EE, EA, and IP). This allowed us to investigate the performance of these approaches and to identify their potential and limitations. We have investigated the performance of cs-EOM-CCSD using small atomic systems; we have found that the strong basis set dependence of the results is due to electron correlation, and not due to the diffuseness of the resonance wave functions, as was previously thought (this work was published in J. Chem. Phys.). Our findings suggest a practical way of developing compact basis sets for resonances. Specifically, we intent to employ Frozen Natural Orbitals technique to develop such bases. We also found that frozen core method provides a reasonable way for dealing with core electron problems.

We have investigated the performance of CAP-EOM-CCSD for various molecular shape resonances. By analyzing analytic energy expression, we discovered a simple yet efficient de-perturbative correction that eliminates the unphysical perturbation due to the finite-strength CAP. This new version of CAP-EOM-CCSD has shown robust performance, improved accuracy, and, in particular, decreased dependence on the CAP onset parameter. We also tested this approach for potential energy curves. Unlike the original versions of CAP methods, our 1st order corrected CAP-EOM-CCSD yields smooth and internally consistent potential energy curves. The results have been published in J.Chem. Phys. (1 paper) and J. Phys. Chem. Lett. (2 papers).

We extended the methodology to describe properties of resonance states by implementing Dyson orbitals and transition dipole moments; this is the first implementation of this kind. The results published in J. Chem. Phys.. We also applied this methodology to interpret the experimental results on resonances in AgF- and CuF-; in these systems we discovered new type of electronic structure, dipole-stabilized shape resonances. The results were published in J. Phys. Chem. Lett.

As far as applications are concerned, one exciting finding is that we have found a new stable form of molecular solid made of nitrogen (N8). This might be of interest to high-energy compounds. The results of this work have been published in Nature Chemistry.

Our work on resonances was recognized by Phi Kappa Phi faculty Recognition Award in 2016. The nomination to the award, which describes our contributions to the theory of metastable states, is attached.

Technology Transfer

The codes developed under the ARO support are integrated into the Q-Chem package. There were released in Q-Chem 4.0. The modules are also available as open source (upon request) and can be integrated in other packages (integration in Cfour and Psi4 is planned).

(4) Scientific Progress and Accomplishments (description should include significant theoretical or experimental advances)

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Metastable electronic states: New advances on the old frontier

Figure 1: In high-energy environments, electrons have sufficient energy to overcome their attraction to the nuclei giving rise to the fourth state of matter called plasma. Plasma consists of charged particles (electrons, ions) and metastable atomic and molecular species. If you think plasma is an exotic matter, think twice. Plasma constitutes 99.999 % of the visible universe, as it is the main component of stars. Plasma is often generated by electric discharge such as in thunderbolt or in plasma TVs. Cosmic radiation produces plasmas in atmosphere giving rise to northern lights.

What are metastable electronic states? These refer to atoms and molecules that cannon hold all their electrons and decay by ejecting an electron, via so called auto-ionization process. They are transient species that have finite lifetime. Yet, they play a crucial role in science and technology. These states are ubiquitous in a fourth state of matter, plasma, which can be generated in high-energy environment (stars, electrical discharge, cosmic radiation, see Fig. 1). They also appear when molecules are exposed to radiation or interact with metal surfaces, e.g., in molecular electronics. Electronic resonances can serve as doorway states in processes such as catalysis, interstellar synthesis, and DNA damage.. They are also commonly encountered in experiments using advanced light sources.

Despite their importance, theoretical description of such metastable states has been elusive. Many prominent theoreticians have worked on this problem since the dawn of Quantum Chemistry. Many ingenuous ideas have been put forward, however, they have not result in practical methods due to the complexity of the many-electron nature of the problem and the importance of electron correlation.

Krylov's group began to work on this problem in 2012. Krylov realized that equation-of-motion coupled-cluster framework, a powerful approach to excited-states and open-shell systems, provides an ideal platform for building the theory for resonances. The series of the 5 papers[1–5] present the realization of the approach and illustrate its capabilities. The essential advance was to realize how to achieve the stabilization of a metastable state by the so-called complex absorbing potential, such that its wave function can be computed, and then remove the perturbation (due to the complex absorbing potential) by deperturbing correction.[3] This lead to the robust performance and reliable results. The new approach enables description of not only atomic, but also molecular resonances and yields potential energy surfaces which are smooth and internally consistent.[4] These tools enabled the discovery of the new type of resonances, dipole-bound shape resonances, which is presented in the last paper in the series. The calculations by Krylov and Jagau revealed that molecules with large dipole moments (like CuF and AgF) can support shape resonances resembling dipole-bound anionic states.[5] In these states, the extra electron resides outside of the molecular core, leading to the distinctly different properties. For example, the lifetime of such s shape resonances is not affected by molecular vibrations, in sharp contrast to the regular shape resonances, as illustrated in Fig. 2.
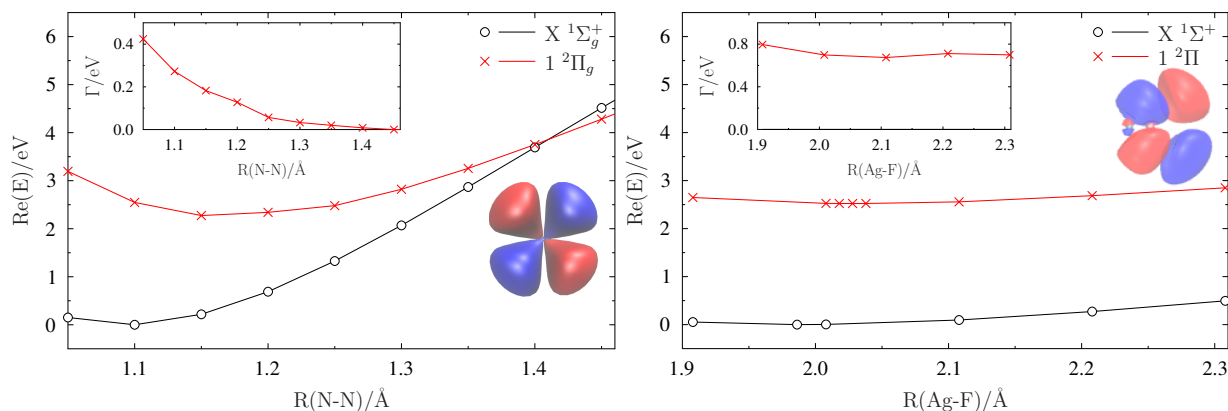
Figure 2: Comparison of regular shape and dipole-stabilized resonances by means of potential energy curves for the $1\,^2\Pi_g$ resonance of N_2^- and the X $^1\Sigma_g^+$ ground state of N_2 (left, data from Ref. 4) and for the $1\,^2\Pi$ resonance of AgF^- and the X $^1\Sigma^+$ ground state of AgF (right, Ref. 5). Resonance widths as a function of bond distance are displayed as insets. Also shown are the molecular orbitals occupied by the excess electron in the resonance states. Regular shape resonances in diatomic molecules such as in N_2^- are stabilized at stretched geometries; the energy of the attached state drops below that of the neutral and its width becomes zero, which can be rationalized by the symmetric shape of the molecular orbital. In contrast, energies and lifetimes of dipole-stabilized resonances, in which the excess electron resides outside the molecular core, remain nearly constant.

Individual contributions. In the 5 papers listed below, Prof. Krylov is the lead theoretical author. The theoretical work presented in these papers has been conducted at USC by Krylov and her postdocs (Bravaya, Jagau, Epifanovsky) and graduate students (Zuev). The contributions of collaborators from Berkeley (Head-Gordon, Sundstrom) and Q-Chem, Inc (Shao) are the computational infrastructure (Q-Chem base code). Prof. Mabbs and his group (Dao, Holtgrewe) conducted experimental measurements.

References

[1] K.B. Bravaya, D. Zuev, E. Epifanovsky, and A.I. Krylov, Complex-scaled equation-of-motion coupled-cluster method with single and double substitutions for autoionizing excited states: Theory, implementation, and examples, J. Chem. Phys. **138**, 124106 (2013).

[2] D. Zuev, T.-C. Jagau, K.B. Bravaya, E. Epifanovsky, Y. Shao, E. Sundstrom, M. Head-Gordon, and A.I. Krylov, Complex absorbing potentials within EOM-CC family of methods: Theory, implementation, and benchmarks, J. Chem. Phys. **141**, 024102 (2014).

[3] T.-C. Jagau, D. Zuev, K.B. Bravaya, E. Epifanovsky, and A.I. Krylov, A fresh look at resonances and complex absorbing potentials: Density matrix based approach, J. Phys. Chem. Lett. **5**, 310 (2014).

[4] T.-C. Jagau and A.I. Krylov, Complex absorbing potential equation-of-motion coupled-cluster method yields smooth and internally consistent potential energy surfaces and lifetimes for molecular resonances, J. Phys. Chem. Lett. **5**, 3078 (2014).

[5] T.-C. Jagau, D.B. Dao, N.S. Holtgrewe, A.I. Krylov, and R. Mabbs, Same but different: Dipole-stabilized shape resonances in CuF^- and AgF^-, J. Phys. Chem. Lett. **6**, 2786 (2015).